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THERMALLY REGENERATIVE FUEL CELLS

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FINAL REPORT
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THERMALLY REGENERATIVE FUEL CELLS

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Description of Project:

The three-phase project was undertaken to investigate solventless ionic liquids as possible working fluids for a new type of thermally regenerative fuel cell (TRFC). The heart of the cell, invented at Hughes Aircraft Company in 1983¹, is an electrochemical concentration cell in which anode and base streams react to produce electrical energy. Thermal energy is then used to decompose the resulting salts and regenerate the cell reactants. In principle, a TRFC can be matched to a source of thermal energy simply by selecting working fluids with the appropriate regeneration temperature. However, aqueous working fluids (the focus of previous studies) impose limitations on the operating temperatures and the achievable energy densities. It was the need to overcome these limitations that prompted the present investigation. Specific aims were to identify possible working fluids for TRFC systems with both low (< 200°C) and high (> 700°C) regeneration temperatures.

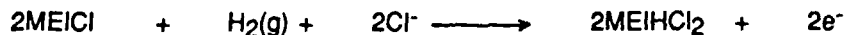
Phase I

A major advantage of our aqueous-fluid TRFC systems has been the ability to use porous carbon electrodes. The low activation and mass transfer losses of these electrodes contribute to overall system efficiency. Professor Robert A. Osteryoung pointed out that this advantage could be extended to molten salt (ionic liquid) systems by using mixed Lewis and Brønsted acids. Based on his own work with low-melting point molten salts, he suggested that we use the fluid system HCl/1-methyl,3-ethylimidazolium chloride (HCl/MEICl). In this system, the following reactions are:

Cathode:



Anode:



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Hydrogen gas is recycled from cathode to anode compartments and chloride ions pass through the (anionic) cell membrane in the same direction. Thermal regeneration occurs by distillation of the HCl out of the spent anode fluid: the HCl is returned to the cathode and the fresh MEICl goes back to the anode.

Test results demonstrated that a TRFC based on HCl/MEICl is capable of operating with a heat source at 200°C, and a cell temperature of about 100°C. In a test where hydrogen transfer from cathode to anode took place by diffusion through the cell membrane, we measured an open circuit voltage (OCV) of 206 mV and a maximum power density of 0.35 mW/cm². Although ten-times larger power densities are commonplace with aqueous TRFC cells, this is the best result we have achieved with through-membrane hydrogen transfer. When hydrogen was fed to the edge of the anode instead, the OCV was 300 mV and the maximum power density was 0.69 mW/cm².

Details of the work were published in the annual contract report for 1990. Problem areas identified during Phase I included possible decomposition of MEICl during regeneration at 200-250°C, incomplete wetting of the fuel cell anode, poor membrane conductivity and the difficulty of separating HCl gas from hydrogen. These areas became the focus of our work during Phase II.

Phase II

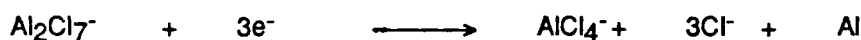
Differential scanning calorimetry (DSC) on a sample of MEICl showed that thermal decomposition began at about 260°C. The result was consistent with published findings that the compound is stable below 250°C². DSC could not be performed on MEIHC1₂ because the compound attacked the sample holder. Instead we analyzed the gases evolved under simulated regeneration conditions. Irreversible decomposition was confirmed at 200-250°C. The decomposition occurred by loss of alkyl groups rather than by ring opening. It could probably be suppressed by replacing the methyl and ethyl groups with larger, more stable substituents such as butyl or propyl groups.

Electrode wetting was improved by reducing the TFE content of the fuel cell anode but no adequate solutions were found to the problems of gas separation or membrane resistance.

Phase III

In view of the performance limitations associated with the HCl/MEICl system, the possibilities of other working fluids were explored. In particular, Lewis acid/base systems of the type AlCl_3/MCl appeared to merit investigation. In this system, the electrode reactions are:

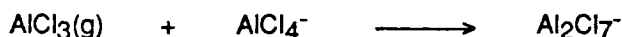
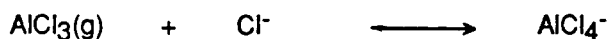
Cathode:



Anode:

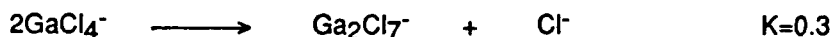


Chloride ions pass through the cell membrane from cathode to anode compartments. Thermal regeneration occurs by distilling AlCl_3 out of the spent anode fluid and returning it to the catholyte:



A disadvantage of the above scheme is the need to return a solid reactant (metallic aluminum) from the cathode to the anode during cell operation. The transfer would be more practical with a liquid reactant such as metallic gallium. For this reason, we chose the model system $\text{GaCl}_3/\text{MEICl}$ to explore the feasibility of a Lewis acid/base working fluid. Funding constraints during 1991 limited the scope of the investigation to a literature review and some preliminary experiments.

We found no published information on the EMF of $\text{GaCl}_3/\text{MEICl}$ concentration cells but such data do exist for the aluminum system³. By comparing the equilibrium constant published by Verbrugge and Carpenter (1990)⁴ for the reaction:



with the equilibrium constant quoted for the corresponding AlCl_3 reaction, ($K=10^{-16}$), we estimated that the EMF of TRFC based on $\text{GaCl}_3/\text{MEICl}$ may reach a few hundred millivolts, with a regeneration temperature in the range 100-200°C.

Concentration cell tests were performed at room temperature in an inert atmosphere glove box. To assemble the cell, an anion-conducting membrane (Pall RAI R-1030) was clamped vertically between the two halves of a split 5-ml Teflon cup. Platinum wires passing through each side of the cup made contact with 1-ml pools of gallium in the bottom of each compartment. Mixtures of GaCl_3 and MEICl of different ratios were placed in the two compartments and the cell EMF was measured. The measured EMFs for three tests are shown in Table 1.

TABLE 1. EMF OF GaCl₃ CONCENTRATION CELLS

Mole % GaCl₃ In Anode Compartment	Mole % GaCl₃ In Cathode Compartment	CELL EMF, VOLTS
26	86.2	2.07
40	86.1	1.75
60	86.2	0.63

Conclusions

Solventless ionic liquids show promise as possible working fluids for both low and high temperature TRFC systems. During Phase I, HCl/MEICl working fluids were found to be viable candidates for a TRFC system that can be regenerated at about 200°C. The system has the potential for becoming the most efficient and highest power density thermal to electrical energy generating device among competing low-temperature technologies. Challenges remaining to be solved include the possible decomposition of MEICl during regeneration, poor membrane conductivity and the difficulty of separating HCl gas from hydrogen.

The surprisingly large EMF values observed with GaCl₃/MEICl cells are very encouraging. They suggest that a TRFC operating on Lewis acid/base fluids may achieve energy densities several times greater than those achievable with aqueous fluids. At the same time, the regeneration temperature is likely to approach 1000°C. While this temperature is clearly too high for organic reagents, substituting NaCl for MEICl may well yield a practical high-temperature TRFC system.

References

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